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Chemkar PM10: An extensive look at the local differences in chemical composition of PM10 in Flanders, Belgium

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ABSTRACT

The results of *Chemkar PM10*, the first large scale chemical characterisation project of PM10 in Flanders are presented. Between September 2006 and September 2007 a total of 365 PM10 samples were collected by sampling every sixth day at six different sites in Flanders (Belgium) varying in character from urban background to rural. Samples were analysed for a series of elements, elemental and organic carbon, $^{13}C/^{12}C$- and $^{15}N/^{14}N$-isotopic ratios, and water-soluble ions. At three sites extra sampling was carried out to determine PAHs by means of a novel technique that uses sorption tubes consisting of polydimethylsiloxane (PDMS) foam, PDMS particles and a TENAX TA bed. Results showed that the most important fractions were secondary inorganic ions (nitrate, sulphate and ammonium): 41% (12.6 $\mu g\,m^{-3}$), organic matter: 20% (6.1 $\mu g\,m^{-3}$), crustal matter: 14% (4.3 $\mu g\,m^{-3}$), sea salt: 8% (2.4 $\mu g\,m^{-3}$) and elemental carbon: 4% (1.2 $\mu g\,m^{-3}$). Although the general composition profile was rather similar for the six sites, substantial differences could be observed for some main components and for several trace metals such as chromium, copper, zinc, arsenic and lead. Although the average sum of the "PAH 16" was quite variable between the three sites (between 132 and 248 $ng\,m^{-3}$) the average sum of the "PAH 7" was between 7 and 9 $ng\,m^{-3}$ for the three sites. The largest relative differences between sites were found for elemental carbon and crustal matter, thereby indicating that there is some potential for local measures to reduce the concentrations of particulate matter by a few $\mu g\,m^{-3}$. Both for carbon and nitrogen isotopic ratios significant differences in time were observed. Isotopic differences in location could only be detected for carbon.

1. Introduction

Particulate matter (PM) is currently the most important compound that determines air quality in large parts of Europe. Although the first European limit values for PM10 were adopted in 1999 (1999/30/EC) many regions are still having a hard time meeting them, even despite the fact that the new directive (2008/50/EC) has become somewhat less stringent (Brunekreef and Maynard, 2008) by maintaining the limit values but allowing additional subtractions of certain natural compounds (e.g. sea salt). Especially the fact that no more than 35 exceedances of the daily limit value for PM10 (50 $\mu g\,m^{-3}$) are allowed, appears to be an issue. One of the problems in reducing PM10 levels is the lack of sufficient information about the importance of the different sources. Because the current routine monitoring networks are generally set up to measure PM10 and PM2.5 mass concentration (as required by the legislation), they often generate data that do not allow to calculate the importance of different sources. A second problem is the complex nature of the aerosol mixture. PM10 is known to be made up of a whole range of compounds that can be traced back to an even larger range of sources. Many of these compounds have contributions in the range of, or even below, a few $\mu g\,m^{-3}$ which makes that differences in their concentrations (in time and place) are hard to detect. To address these issues the Flemish Environment Agency decided to operate a PM10 chemical characterisation network during one full year. The general setup focussed on the determination of a whole range of elements, elemental and organic carbon (EC/OC) and water-soluble ions. Additionally, PAH concentrations and isotopic ratios of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) were measured. Although this type of research had on occasion been

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done in Flanders it was always limited in time and space (Putaud et al., 2004; Viana et al., 2007; Maenhaut, 2007; Ravindra et al., 2008). Apart from the main goal to identify the importance of various (groups of) sources, the data of this study were also used for model validation. In addition the work could also be seen as a test-case for the new EU legislation 2008/50/EC that, for the first time, legally requires Member states to monitor EC/OC and certain water-soluble ions in PM2.5 at rural background sites.

2. Experimental

2.1. Sampling sites

Sampling was done at six sites in Flanders, Belgium (Fig. 1). The sites were chosen to obtain a reasonable spread in location and type of site. The six sites were located in Houtem (rural background), Zelzate (industrial), Mechelen (suburban), Borgerhout (urban background), Aarschot (rural background) and Hasselt (suburban). Additionally, 8 extra samples were taken in December 2007 in the Waasland tunnel in Antwerp.

2.2. Sampling, weighing and storage

From September 2006 to September 2007 24-h sampling was carried out simultaneously on all locations on every 6th day with two PM10 low-volume samplers (Leckel SEQ 47/50). Filters were automatically changed in the sampler at 23 h55 UT. With this setup 55 m^3 of air was sampled on both a quartz fibre (pre-fired Whatman QM-A) and a teflon filter (Pall Teflo 2 μm). PM mass was determined with a Sartorius M5P balance at 20 °C and 50% RH according to the European PM2.5 standard EN14907 (which prescribes double weighings before and after the sampling). After the last weighing the quartz fibre filters were cut in two parts. About one third was stored at −18 °C until analysis for EC/OC and C- and N-isotopic ratios. The remaining part of the filter was stored at +4 °C until analysis for water-soluble ions. Teflon filters were kept at weighing room temperature (20 °C) and used to determine a range of elements by means of XRF. Additionally PAHs were sampled at three of the six locations, i.e. Zelzate, Borgerhout and Aarschot.

2.3. Chemical analysis

For EC/OC determination a 1 cm^2 punch was analysed by means of a thermal-optical transmission (TOT) method with a Sunset Laboratory (Tigard, OR, USA) Lab OCEC analyser using the NIOSH 5040 protocol (Birch, 1996). The remaining part of the quartz filter was leached in 5 mL of Milli-Q water in an ultrasonic bath (Bransonic 2210, Branson, Danbury, CT, USA) using 10 min trembling time. The solutions were filtered by a Millex-GV Syringe Driven Filter Unit 0.22 μm (Millipore, Carrigtwohill, Co. Cork, Ireland) and put into 2 mL vials (Dionex, Sunnyvale, USA) for ion chromatography analysis of NO_3^-, Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. A Dionex Model DX-120 ion chromatograph equipped with Dionex IonPac CS12A cation and Dionex IonPac AS14 anion exchanger columns and a conductivity detector was used. For sample introduction, the solutions were injected through a 20 μL loop with a Dionex AS-50 autosampler. The eluents for the anion and cation exchangers were solutions of 3.5 mM Na_2CO_3 plus 1.0 mM $NaHCO_3$ and 11 mM H_2SO_4, respectively, flow rates were 1.2 mL min^{-1} and 1.0 mL min^{-1}, respectively. For the conductivity suppression of the eluents, the ASRS-ULTRA and CSRS-ULTRA (Dionex) suppressors were used. Element analysis was done with an ED-XRF spectrometer Epsilon 5 from PANalytical (Almelo, The Netherlands). The following elements were measured: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rh, Pd, Cd, Pt, Pb and Se. Isotopic ratios of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) were measured on a second 1 cm^2 punch taken out of the smallest quartz filter part. The method used was Elemental Analysis − Isotope Ratio Mass Spectrometry (EA-IRMS). This is the common method for the measurement of nitrogen and carbon stable isotopes in solid bulk materials. The instrument used was an EA-Deltaplus from Thermo (Bremen, Germany). A detailed description of the method is given in a report by Mikolajczuk et al. (2006). In short, approximately 1 cm^2 of quartz filter containing the PM10 sample was weighed and put into a tin foil capsule (Iva Analytic, Meerbusch, Germany), which is folded to hold the sample. Sample weight including filter material was around 10 mg. In the online continuous flow analysis the sample is oxidized and oxidation gasses are partially reduced, after which the resulting gasses, carbondioxide for the C isotopic analysis and nitrogen gas for the N isotopic analysis, are lead to the mass spectrometer in a constant flow of helium. In this isotope ratio mass spectrometer the different isotopic species of the gas are separated and detected, resulting in isotopic ratio data expressed as a δ-value. All measurements are done in comparison to a working reference, since IRMS is a differential system. These references were pure gasses (Air Liquide) calibrated against internationally agreed reference substances (NBS19 and L-SVEC for carbon and USGS32 and IAEA-N1 for nitrogen). General uncertainty in δ-values is estimated to be 0.2‰, for carbon as well as nitrogen. Analysis shows no carbon or nitrogen present in blank filter material as expected since this is quartz. PAH sampling and analysis was done according to a new method described by Wauters et al. (2008). In short the method is based on active sampling on sorption tubes consisting of polydimethylsiloxane (PDMS) foam, PDMS particles and a TENAX TA bed. After sampling, the solutes are quantitatively recovered by thermal desorption and analysed by capillary GC−MS.

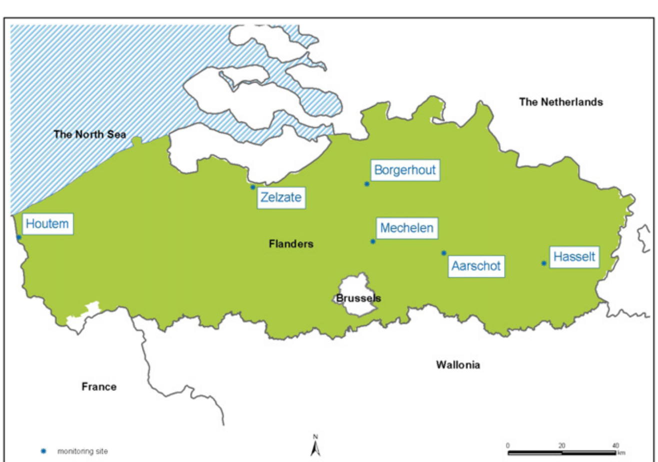

Fig. 1. Location of the 6 monitoring sites in Flanders, Belgium.

3. Main results

3.1. PM10 and main components

An overview of the total PM10 mass concentrations for the full study is given in Fig. 2. Because of the relatively small distance between the sites, PM10 concentrations were often highly correlated. They did however vary greatly from day to day, ranging from below 10 μg m^{-3} up to almost 100 μg m^{-3}. Average concentrations for PM10 mass (on both teflon and quartz), EC, OC and the soluble ions are given in Table 1. Using the following formulas the

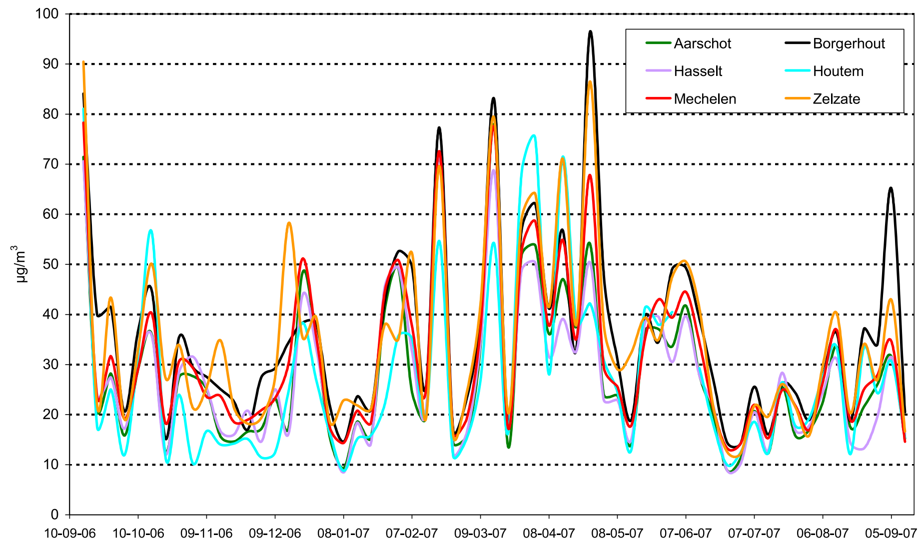

Fig. 2. Overview of the PM10 mass concentrations, as derived from the quartz fibre filters, for all stations.

contribution of the main fractions was calculated (Fig. 3), whereby $nssSO_4^{2-}$ stands for non-sea salt-sulphate.

- Organic mass (OM) = 1.4 OC.
- Crustal matter = 2.20 Al + 2.49 Si + 1.63 Ca + 2.42 Fe + 1.94 Ti.
- Sea salt = Cl^- + 1.45 Na^+.
- $nssSO_4^{2-} = SO_4^{2-} - 0.231\ Na^+$.

The equations for OM, crustal matter, and sea salt are identical to those used by Maenhaut et al. (2002).

Although the general picture in Fig. 3 is quite similar for the six sites, some significant differences could be observed. The relative differences to the overall average are presented in Fig. 4. The largest difference was observed for EC. The average concentration (2.04 µg m^{-3}) at the urban background site in Borgerhout, located 30 m from a busy road, was about 4 times higher than at the rural site in Houtem (0.47 µg m^{-3}), indicating the very local character of this fraction. Also for crustal matter large local differences were observed. The highest averages were recorded in Borgerhout and Zelzate (6.24 µg m^{-3} and 6.06 µg m^{-3} respectively) and were about 3 times higher than those in Houtem (2.17 µg m^{-3}). Together with EC these differences seem to indicate that traffic is an important local source for PM pollution. For sea salt, the concentration decreased with distance from the North Sea, from 2.98 µg m^{-3} in Houtem to 1.80 µg m^{-3} in Hasselt. Relative differences for OM and major ions were small, showing the secondary character of these fractions. However, in absolute numbers the differences are important, as demonstrated by an average difference between Zelzate and Hasselt of 3.68 µg m^{-3} for the sum of nitrate, sulphate and ammonium and an average difference between Houtem and Borgerhout of 2.88 µg m^{-3} for OM.

3.2. Crustal and trace elements

The average concentrations for the elements that were analysed with XRF are given in Table 2. For some elements all the data were multiplied with an ICP-MS/XRF correction factor that was determined on a dozen of filter samples. After the standard XRF analysis of the filter, the filters were digested and analysed with ICP-MS (which was done by a commercial lab). The factors were 0.74 for Al, 1.27 for Fe, 0.97 for Si, 0.27 for Ti, 0.99 for K, 1.00 for Ca and 0.70 for Mn. Although it is known that acid digestion with the use of HF and subsequent ICP-MS analysis can lead to incomplete recoveries for certain elements (Kulkarni et al., 2007) we considered the ICP-MS results as the 'best available' values. Although the applied correction is open for discussion (especially the factor for Ti seems low), its effect on the calculation of crustal matter is very limited (on average +4%). Using the crustal composition data of Taylor (1964) crustal enrichment factors were calculated by dividing the 'element to Al' ratio in our samples by the 'element to Al' ratio in average crustal rock. The average results are presented in Table 3. Values in the order of magnitude of 1 indicate that these elements can largely be attributed to crustal matter. The higher the enrichment factor, the more important other sources are. As expected, typical crustal elements such as Si, Fe, Ca, Mn and Ti have enrichment factors close to one and most other elements have (much) higher enrichment factors, indicating that other sources are at play. For Fe there seems to be additional enrichment at the industrial site in Zelzate, which is located about 2 km from a large metal processing plant. Ti is the only element with a factor below 1, which could be due to overcorrection of the XRF results with the ICP-MS/XRF factor. For V a clear trend from West to East can be observed (65 in Houtem to 14 in Hasselt). A similar trend could be observed

Table 1
Average concentrations for PM10, EC, OC and soluble ions for all sites in µg m^{-3}. $PM10_T$ denotes PM10 mass concentrations, as derived from the teflon filters, and $PM10_Q$ is as derived from the quartz fibre filters.

	$PM10_T$	$PM10_Q$	OC	EC	NO_3^-	Cl^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Houtem	27.2	27.4	3.21	0.47	7.04	1.43	3.31	1.07	2.04	0.51	0.11	0.24
Zelzate	34.2	35.0	4.43	1.31	8.00	1.46	4.33	0.95	2.47	0.67	0.11	0.35
Mechelen	28.2	31.6	5.05	1.30	6.51	0.92	3.84	0.83	2.10	0.54	0.08	0.25
Borgerhout	33.7	35.7	5.27	2.04	7.59	1.14	4.19	0.97	2.31	0.57	0.10	0.31
Aarschot	27.6	28.2	4.07	0.98	6.18	0.75	3.68	0.74	2.08	0.52	0.08	0.23
Hasselt	27.2	27.8	4.28	1.18	5.55	0.74	3.68	0.73	1.87	0.45	0.09	0.25
All stations	**29.7**	**30.9**	**4.38**	**1.21**	**6.81**	**1.07**	**3.84**	**0.88**	**2.14**	**0.54**	**0.10**	**0.27**

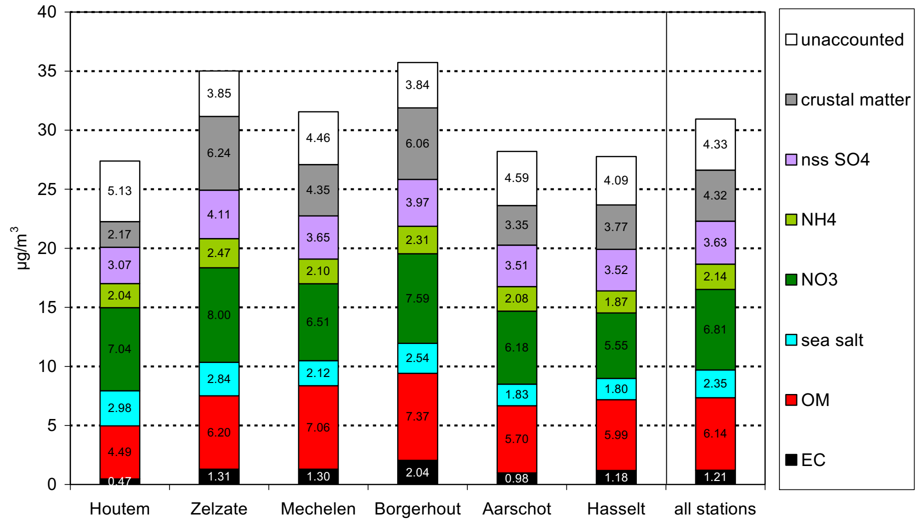

Fig. 3. Average concentrations of the main fractions in PM10 for all stations.

for Ni (41 for Houtem to 18 for Hasselt). Since both V and Ni are tracers for heavy fuel oil combustion (e.g., Sippula et al., 2009), it appears that either the petrochemical industry in Dunkerque (located at only 15 km from the Houtem site) or possibly the shipping traffic on the North Sea are the most important sources for these metals in Flanders. These hypotheses seem to be confirmed by the fact that the median V/Ni ratio clearly reduces from west to east: from 2.8 in Houtem to 1.7 in Hasselt. Although Viana et al. (2009) found V/Ni ratios (for PM2.5) in the range of 2.5–5 to be an indication for shipping emissions it cannot be excluded that petrochemical industry gives similar ratios. For Cu there are also substantial differences in enrichment factors, ranging from 171 at the urban site in Borgerhout to 69 at the rural site in Houtem. In combination with the overall correlation between Cu and EC ($r = 0.89$ for the full dataset) it is highly likely that traffic, i.e. the wearing of brake pads (e.g., Garg et al., 2000; Weckwerth, 2001; Pakkanen et al., 2003) is the main source of Cu in Flanders. For As the higher average concentration and higher enrichment factor in Borgerhout were due to a handful of very high concentrations (up to 300 ng m^{-3}) on this site. The average As concentrations should be considered as indicative since there is a high uncertainty on the XRF values (which were often close to or below the detection limit) and since they are only based on 61 sampling days, which might not be representative for the real annual average of a parameter with such high daily variations. Nonetheless they do indicate that some important As pollution events did occur in the timeframe of this study. Similar As events were reported by the routine heavy metal monitoring network in Flanders at a site in Hoboken, only a couple of kilometres away from the site in Borgerhout (VMM, 2009).

3.3. Factor analysis

Additional statistical analysis was done by means of factor analysis with the Statistica software (StatSoft, Inc., Tulsa, USA). The dataset was first screened for extreme cases. Seven cases were excluded (of which four in Zelzate) as they were considered ‘not representative for the full dataset’. As and P were left out of the analysis since the XRF data for both elements had high uncertainties and elevated values occurred at only one single site (Zelzate for P and Borgerhout for As). A varimax rotation was used to

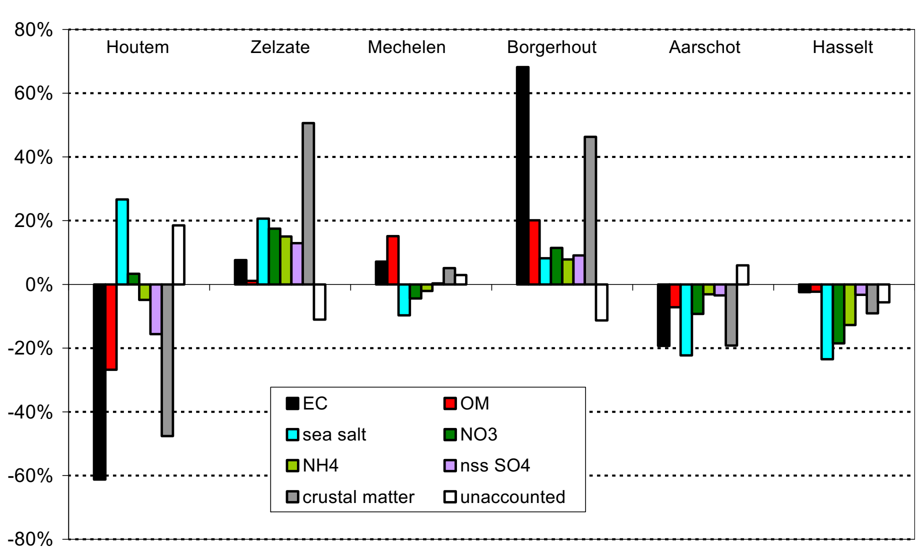

Fig. 4. Local, percentage concentration differences for the main fractions compared to the overall averages.

Table 2
Average concentrations of the elements determined for all stations in ng m^{-3}.

	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Houtem	100	340	40	1790	1400	187	250	2.8	10.6	1.6	6.9	286	3.8	4.6	37	0.7	12.0
Zelzate	178	724	108	2230	1430	310	638	6.5	11.1	2.9	12.1	1240	4.7	13.5	50	1.1	32.0
Mechelen	195	655	46	2160	846	246	401	5.6	6.3	3.7	8.3	674	3.5	15.8	66	1.2	19.0
Borgerhout	215	828	40	2250	1110	249	613	6.5	9.6	4.5	10.5	1040	4.6	24.6	72	17.5	27.0
Aarschot	143	527	40	2060	751	218	317	4.1	4.7	3.4	7.2	495	2.6	10.7	74	1.2	16.0
Hasselt	154	547	36	2010	726	211	346	4.3	3.5	5.0	8.3	618	2.5	16.1	101	0.9	17.0
All stations	**164**	**603**	**52**	**2080**	**1050**	**237**	**427**	**5.0**	**7.6**	**3.5**	**8.9**	**725**	**3.6**	**14.2**	**67**	**3.8**	**21.0**

simplify interpretation. An analysis was done for each of the six locations separately and for the data from the six locations combined (full dataset). The results were in general quite comparable. Therefore, only the results of the analysis with the full dataset analysis are given here (Table 4). Five factors, which explain at least one unit of variance, were retained. Combined they explained 86% of the total variance. The factors can be explained as follows:

- Factor 1 (Ca^{2+}, Al, Si, K, Ca, Ti, Mn, Fe): crustal matter
- Factor 2 (Cl^-, Na^+, Mg^{2+}, Cl): sea salt
- Factor 3 (OC, NO_3^-, SO_4^{2-}, NH_4^+, K^+, S): secondary aerosol
- Factor 4 (OC, EC, Cr, Mn, Fe, Cu, Zn, Pb): traffic and metals
- Factor 5 (V, Ni): heavy oil burning

For the factor ‘crustal matter’ it is quite interesting to note that elemental K has a high loading, but ionic K^+ does not. The latter is however highly loaded on the factor of the secondary aerosols. Factor 4 appears to be a mix of traffic related species and elements (EC, OC, Cu, Fe, Cr) and some other (heavy) metals.

The only other important local exception to this overall picture was observed at the industrial site in Zelzate, were a separate factor representing a specific type of mineral dust with high loading for K, Ti, Mn, Fe, Zn and Pb was found, indicating that on this site there was an additional source for these elements.

4. Additional calculations and discussion

4.1. Sea salt contribution

The current European directive (2008/50/EC) states that the European Commission will not take into account exceedances of the limit value that can be attributed to ‘natural sources’ such as sea salt. This makes the calculation of ‘natural’ sea salt an often debated issue. Although different formulas based on the composition of sea water (e.g. Turekian, 1968) are being used, none can be considered perfect. The problem is that the two best tracers for sea salt, Na^+ and Cl^- both have drawbacks. Na^+ can also arise from crustal matter and is often associated with nitrate due to ageing of sodium chloride by reaction with nitric acid (in which chloride is lost as gaseous HCl). As a consequence, estimating sea salt from the often used formula of 3.24 Na^+ will certainly lead to an overestimation of ‘natural’ sea salt. That the reaction of sea salt with nitric acid is significant in Flanders can be deduced from the decrease in Cl^-/Na^+ ratio with distance from the coast (Table 5). Since the nitric acid in our region is almost entirely from anthropogenic origin sodium nitrate cannot be considered a ‘natural’ compound. Chloride, on the other hand, can also come from industrial sources. The fact that the Cl^-/Na^+ ratios in our study are equal to or lower than the Cl^-/Na^+ ratio of 1.8 in sea water indicates that the loss of Cl^- is more important than the possible industrial emissions. This also means that a formula like 1.8 Cl^- will lead to an underestimation of sea salt. To deal with the facts above, an intermediate approach is often used in which one of the two ions is used to calculate the fraction of sea salt without the other ion. To do this, there are two options: 1.45 $Na^+ + Cl^-$ or $Na^+ + 1.26\ Cl^-$. The results obtained with the different formulas are presented in Table 5. As expected, 3.24 Na^+ gives the highest sea salt estimate, on average, 9.2% of the PM10 mass, followed by 1.45 $Na^+ + Cl^-$ with an average of 7.6% of the PM10 mass, then $Na^+ + 1.26\ Cl^-$ with an average of 7.2% of the PM10 mass, and the lowest estimate of 6.2% is found with 1.8 Cl^-. Since the main problem of exceedances of the limit value is the number of days with PM10 mass concentration above 50 μg m^{-3} we split the dataset in two parts, one large set ($n = 318$) containing all cases where the PM10 mass was below 50 μg m^{-3} and one smaller dataset ($n = 47$) containing all cases where the PM10 mass was above the daily limit value. We found that the average concentrations of chloride and sodium on non-exceedance days were 1.13 and 0.91 μg m^{-3} respectively, and were 71% and 26% higher than on exceedance days (0.66 and 0.72 μg m^{-3}). This can be explained by the fact that very few exceedances occur on days with transport of marine air over Flanders. The fact that the difference between the two datasets is much larger for chloride than for sodium also shows that the salt that is present on exceedance days is clearly much more aged than on non-exceedance days. Using the full dataset (with 365 cases) we estimated the effect of sea-salt subtraction on the number of ‘yearly’ exceedances throughout Flanders. Depending on the formula that was used a reduction between 8 and 4 exceedance days per site was found. However, we do have to stress that this will probably be different from year to year, as the only cases that are affected are the ones with PM10 mass concentrations just above 50 μg m^{-3} and their number will likely vary depending, e.g., on meteorological conditions.

Table 3
Average crustal enrichment factors (using Al as reference element) for the measured elements.

	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Houtem	1.0	32	5670	8900	7.4	5.0	0.4	65	13	6.0	4.2	41	69	439	319	778
Zelzate	1.2	47	3950	5100	6.9	7.1	0.5	38	13	5.9	10.1	29	113	332	285	1189
Mechelen	1.0	19	3520	2750	5.0	4.1	0.4	20	15	3.7	5.1	20	121	401	294	653
Borgerhout	1.1	15	3320	3270	4.6	5.7	0.4	27	17	4.2	7.1	23	171	395	3731	827
Aarschot	1.1	22	4560	3330	6.0	4.4	0.4	20	20	4.3	5.1	20	112	608	372	734
Hasselt	1.0	18	4120	2980	5.4	4.4	0.4	14	27	4.7	5.9	18	157	767	265	727
All stations	**1.1**	**25**	**4020**	**4030**	**5.7**	**5.2**	**0.4**	**28**	**18**	**4.7**	**6.5**	**24**	**130**	**479**	**1052**	**824**

Table 4
Varimax rotated Factor Loadings for a factor analysis on the complete dataset. Loadings for which the absolute value is larger than 0.5 are indicated in bold.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Variance explained	*21%*	*16%*	*20%*	*19%*	*9%*
OC	0.40	0.16	**0.51**	**0.62**	0.07
EC	0.19	0.14	0.02	**0.83**	0.18
NO_3^-	0.23	−0.03	**0.74**	0.18	0.46
Cl^-	−0.13	**−0.95**	−0.11	−0.15	−0.02
SO_4	0.23	0.15	**0.89**	0.16	0.08
Na^+	0.01	**−0.91**	−0.11	−0.24	0.05
NH_4^+	0.16	0.03	**0.87**	0.22	0.33
K^+	0.20	0.05	**0.88**	0.24	0.29
Mg^{2+}	0.01	**−0.95**	−0.01	−0.05	0.04
Ca^{2+}	**0.63**	−0.35	0.38	0.29	0.17
Al	**0.91**	0.13	0.20	0.14	0.01
Si	**0.91**	0.15	0.23	0.15	0.06
S	0.20	0.22	**0.86**	0.15	0.05
Cl	−0.13	**−0.93**	−0.12	−0.16	−0.03
K	**0.70**	−0.06	0.39	0.43	−0.06
Ca	**0.79**	0.04	0.01	0.28	0.20
Ti	**0.82**	0.08	0.23	0.28	0.10
V	0.12	−0.06	0.36	−0.03	**0.89**
Cr	0.27	0.19	0.18	**0.71**	−0.09
Mn	**0.55**	0.08	0.21	**0.58**	0.18
Fe	**0.55**	0.07	0.10	**0.67**	0.23
Ni	0.17	0.01	0.39	0.25	**0.83**
Cu	0.25	0.17	0.09	**0.81**	0.17
Zn	0.04	0.13	0.21	**0.75**	−0.11
Pb	0.28	0.01	0.35	**0.68**	0.09

4.2. Analysis of tunnel samples

In addition to the normal campaign we had the opportunity to sample some extra quartz fibre samples in the Waasland tunnel in Antwerp. This tunnel is a busy access road into the city and is 2 km long and 9 m wide. Due to the very high PM10 mass concentrations (between 147 and 419 $\mu g\, m^{-3}$) 24 h of sampling was never obtained. The instrument could not handle the high backpressure and shut down automatically, resulting in between 24 and 28 m^3 of sampled air. Since there were no samples with teflon filters taken in the tunnel, only EC/OC and ion analyses was done. The results are presented in Fig. 5 which also contains the average results of the nearby Borgerhout station and the overall averages of the study. In general the PM10 mass concentrations in the tunnel were about 8 times higher than in the ambient air. On the last 4 sampling days (December 14–17) very high concentrations of Na^+ and Cl^- were observed. On December 15 their sum was almost 150 $\mu g\, m^{-3}$. These concentrations were probably caused by winter salting, which is also supported by the fact that the Mg^{2+} level (0.1 $\mu g\, m^{-3}$) did not show any increase compared to the ambient average in the project. The other ions did not show an increase either, which indicates that there is no additional formation of (secondary) inorganic aerosols inside the tunnel. The largest relative increase compared to the ambient values was observed for EC (on average 27 $\mu g\, m^{-3}$ in the tunnel) which was 22 times higher than the ambient average. Also OC (on average 69 $\mu g\, m^{-3}$ in the tunnel) was much higher, up to 15 times compared to the ambient level. Due to the very high loading of the filters the EC/OC split had to be set manually, which results in extra uncertainty regarding the EC and OC values. Their sum, total carbon (TC) however, is not affected by the setting of the split point, so it is fair to state that the traffic inside the tunnel resulted in an increase of more than an order of magnitude for carbonaceous species. Since water or non-carbon atoms in the organic mass can only explain a minor fraction of the unaccounted mass (on average 102 $\mu g\, m^{-3}$) there is a strong presumption that crustal matter (which was not calculated) was a very important fraction of the tunnel dust. This suggests that the traffic in the tunnel is responsible for very high concentrations of road dust.

Table 5
Calculation of sea salt contribution (in $\mu g\, m^{-3}$) according to different formulas.

$\mu g\, m^{-3}$	3.24 Na^+	1.45 $Na^+ + Cl^-$	$Na^+ + 1.26\ Cl^-$	1.8 Cl^-	Linear regression	r^2
Houtem	3.46	2.98	2.87	2.57	$Cl^- = -0.28 + 1.60\ Na^+$	0.80
Zelzate	3.08	2.84	2.79	2.62	$Cl^- = -0.36 + 1.81\ Na^+$	0.80
Mechelen	2.70	2.12	1.99	1.65	$Cl^- = -0.30 + 1.46\ Na^+$	0.78
Borgerhout	3.14	2.54	2.40	2.05	$Cl^- = -0.39 + 1.53\ Na^+$	0.81
Aarschot	2.40	1.83	1.69	1.36	$Cl^- = -0.29 + 1.42\ Na^+$	0.78
Hasselt	2.37	1.80	1.66	1.33	$Cl^- = -0.18 + 1.26\ Na^+$	0.69
All stations	**2.86**	**2.35**	**2.23**	**1.93**		

4.3. C- and N-isotope analysis

Although isotopic ratios for different sources can vary due to differences in reaction kinetics for the two isotopes, the ratios are seldom straightforward to interpret because both C and N are present in many different forms (as a mix of sources) and aerosol reactions with exchange, addition or loss of C and N atoms can occur (aerosol ageing), all of which can influence the overall isotopic ratio of the sample (Huang et al., 2006). Results of the carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) stable isotope analysis are presented in Figs. 6 and 7, respectively. Concentrations are expressed as "δ" which is the difference in ‰ relative to the international CO_2 standard for C and atmospheric N_2 for N. One can observe that for our samples all $\delta^{13}C$ values are within the range of −30 to −25‰. This is comparable to values reported for Paris by Widory et al. (2004), somewhat smaller than the range found in the UK by Kelly et al. (2005) and wider than the range reported in Canada by Huang et al. (2006). Apart from the variations in time there also appear to be some differences from location to location, with most of the highest values found in Mechelen and most of the lowest values in Houtem, the site with the lowest average OC concentration. When compared to other parameters no relation could be found which makes it hard to explain the results, but which could also indicate that the isotopic ratios contain information that is not available in other parameters. The latter can also be said of the $\delta^{15}N$ results. Although no significant local differences could be observed, the variations in time are quite large resulting in a range from 0 to 20‰, which is higher than the range reported by Kelly et al. (2005).

4.4. PAH analysis

At the Chemkar project sites in Zelzate, Borgerhout and Aarschot samples were taken for subsequent PAH analysis. The summer/winter pattern varied from compound to compound (Table 6). Although there are some exceptions, in general the lighter PAHs show no or only a slight increase in winter, while the majority of the heavier PAHs are present at concentrations up to 2–3 higher in winter. This is an indication that these compounds are mostly emitted by a major source in winter, most likely being domestic heating (combustion of solid fuels) which is known to be a major source of PAHs in Flanders (Van Rompaey et al., 2000). Average summer/winter concentrations of all measured PAHs are presented in Table 6. The highest concentrations are generally found in Borgerhout and the lowest in Aarschot. The relative differences between the concentrations at the two sites are, however, larger for the lighter PAHs and decrease for the heavier

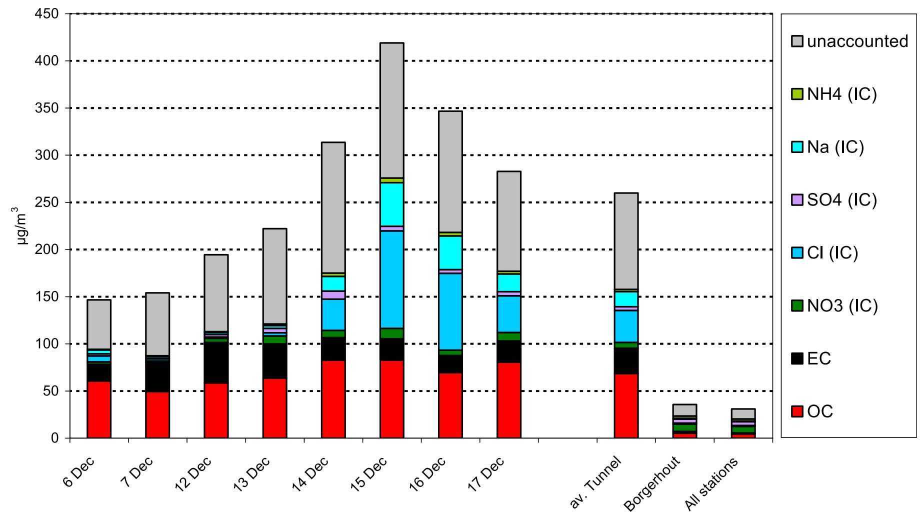

Fig. 5. Concentrations of main components in the Waasland tunnel samples.

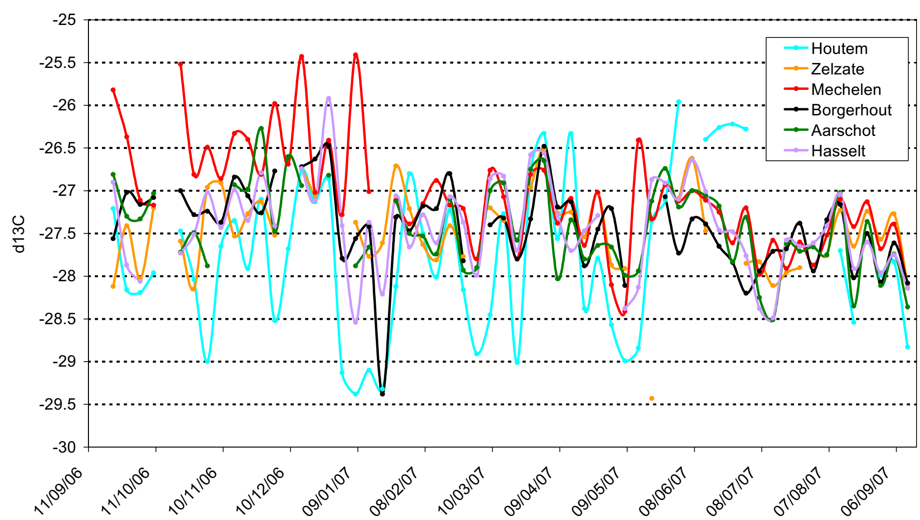

Fig. 6. Results of the C stable isotope ratio measurements for all six sites.

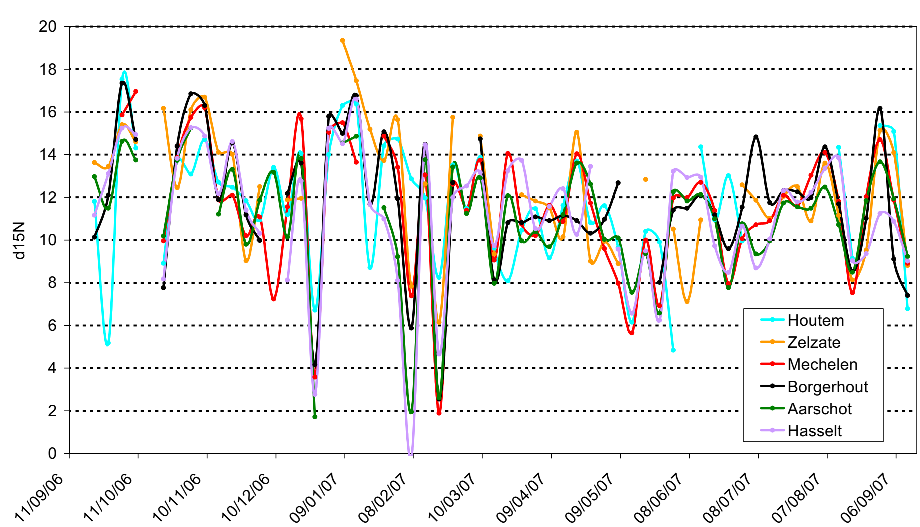

Fig. 7. Results of the N stable isotope ratio measurements for all six sites.

Table 6
Average concentrations of the PAHs (in ng m^{-3}) at Zelzate, Borgerhout and Aarschot.

	Zelzate (Oct–Mar)	Borgerhout (Oct–Mar)	Aarschot (Oct–Mar)	Zelzate (Apr–Sep)	Borgerhout (Apr–Sep)	Aarschot (Apr–Sep)
Naphthalene	146	174	110	109	167	79
Acenaphthylene	3.49	5.31	2.40	1.13	2.21	0.66
Acenafteen	9.3	12.8	6.7	10.9	14.9	5.8
Fluorene	9.4	13.0	7.2	10.3	16.1	7.5
Phenanthrene	17.0	22.7	11.3	13.7	24.4	8.6
Anthracene	1.49	2.06	0.73	0.58	0.95	0.36
Fluoranthene	6.4	7.7	4.6	3.6	6.0	2.4
Pyrene	4.0	5.4	2.8	1.6	3.0	1.1
Benz(a)anthracene[a]	1.25	1.38	0.80	0.43	0.65	0.28
Chrysene[a]	1.96	2.03	1.38	0.62	0.86	0.47
Benzo(b)fluoranthene[a]	3.4	3.5	2.7	1.0	1.5	1.0
Benzo(k)fluoranthene[a]	0.90	0.80	0.71	0.33	0.41	0.35
Benzo(e)pyrene[b]	1.05	1.29	0.80	0.42	0.55	0.38
Benzo(a)pyrene[a]	**0.95**	**1.18**	**0.81**	**0.37**	**0.51**	**0.41**
Dibenzo(a,h)anthracene[a]	0.68	1.06	1.02	0.72	0.82	1.04
Benzo(ghi)perylene	1.15	1.31	1.09	0.60	1.07	0.91
Indeno(1,2,3-cd)pyrene[a]	1.37	2.01	1.66	0.99	1.30	1.35
Sum PAH 16	**209**	**256**	**155**	**156**	**241**	**111**
Sum PAH 7	**10.5**	**12.0**	**9.1**	**4.5**	**6.0**	**4.9**

[a] Belong to PAH 7.
[b] Does not belong to PAH 16.

PAHs. This is an indication that the lighter PAHs are more typical for the urban site of Borgerhout. Analysis also showed that most of the lighter PAHs (naphthalene, acenafteen, fluorine, phenanthrene, anthracene, fluoranthene, pyrene) correlated quite well with Cu and EC ($r > 0.50$) which is a strong indication that traffic is a major source for these compounds. When factor analysis was carried out on the separate summer and winter datasets, two quite different results were found (Table 7). In summer three factors explained 85% of all variance. The different factors divided the PAHs according to molecular mass and both factor 1 (naphthalene to pyrene) and factor 2 (benz(a)anthracene to benzo(a) pyrene) each explained about between 30 and 40% of the total variance. In winter the results were quite different. During this time the first factor contained all PAHs from naphthalene up to benzo(a)pyrene and no distinction was made within this group, indicating that probably one type of source (most likely domestic heating) dominates the PAH emissions during the colder time of year.

Table 7
Factor Loadings for a factor analysis on the separate summer and winter PAH datasets of all three sites. Loadings larger than 0.5 are indicated in bold.

	Summer (Apr–Sep)			Winter (Oct–Mar)		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Variance explained	*38%*	*33%*	*14%*	*60%*	*11%*	*10%*
Naphthalene	**0.85**	0.06	0.00	**0.85**	−0.06	0.25
Acenaphthylene	**0.82**	0.09	0.08	**0.73**	0.05	0.17
Acenafteen	**0.95**	−0.03	0.05	**0.56**	0.03	**0.72**
Fluorene	**0.93**	−0.03	0.20	**0.75**	0.03	**0.62**
Phenanthrene	**0.92**	0.02	0.00	**0.88**	0.00	0.42
Anthracene	**0.76**	0.42	−0.16	**0.85**	0.01	0.36
Fluoranthene	**0.92**	0.28	−0.07	**0.94**	0.01	0.20
Pyrene	**0.85**	0.41	−0.16	**0.94**	−0.01	0.15
Benz(a)anthracene	0.08	**0.94**	−0.10	**0.91**	0.00	−0.20
Chrysene	0.31	**0.90**	0.00	**0.93**	0.05	−0.14
Benzo(b)fluoranthene	0.26	**0.87**	0.25	**0.82**	0.17	−0.32
Benzo(k)fluoranthene	0.09	**0.86**	0.31	**0.81**	0.10	−0.25
Benzo(e)pyrene	0.19	**0.88**	0.15	**0.74**	0.17	−0.24
Benzo(a)pyrene	0.03	**0.94**	0.23	**0.90**	0.18	−0.28
Dibenzo(a,h)anthracene	−0.12	0.19	**0.81**	0.22	**0.80**	0.05
Benzo(ghi)perylene	0.16	0.26	**0.76**	0.40	**0.76**	0.00
Indeno(1,2,3-cd)pyrene	0.02	0.42	**0.86**	0.50	**0.78**	−0.07

5. Conclusions

Flanders is one of the air pollution hotspots in Europe and a better understanding of its air quality is of major importance for local, national and even international policy makers. Although there clearly are regional differences, most of Flanders can be considered as a densely populated region with high industrial activity, an extensive transport network and intensive agriculture. Together with the relatively small size, local differences in PM composition are expected to be relatively small. To be able to detect such small local differences, an extensive research campaign is needed. This one year long study indicates that traffic related components such as elemental carbon and crustal matter exhibit the largest relative differences between the investigated sites, thereby suggesting that there is some potential for measures that target traffic emission on both a local scale (e.g. low emission zones) as for measures that decrease emissions in general (cleaner engines, less traffic,…). Although the relative differences for secondary (in)organic aerosols are small, the absolute numbers are relevant because of their high abundance. Taking into account that ammonium nitrate is, in mass concentration, often the most important compound in Flanders, measures to reduce the precursor gases NH_3 and NO_x could have a significant impact on PM10 levels. Since the formation of ammonium nitrate is often limited by the presence of ammonia (Erisman and Schaap, 2004; Redington et al., 2009) measures that target the agricultural (and possibly traffic) emissions could have a relatively high effect. Whether these measures would also significantly reduce the health effects of PM10 in the region is a harder question to answer. As this research generated much useful information from both a scientific and a policy point of view, a similar campaign was set up at the end of 2008 to characterise PM10 on 5 local hotspots and 2 background sites in Flanders. In early 2010 a new study will also be launched in which the contribution of wood burning is to be addressed.

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